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WASHINGTON STATE UNIV PULLMAN DEPT OF CHEMISTRY

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SYNTHESIS AND SPECTROSCOPIC INVESTIGATION OF INORGANIC MATERIAL--ETC(U)

1979

G A CROSBY

AFOSR-76-2932

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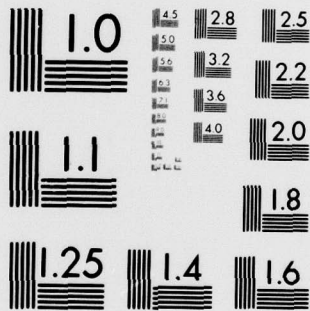
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9 FINAL REPORT 16 Sep 75 - 30 Sep 79

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TITLE: Synthesis and Spectroscopic Investigation of Inorganic Materials Possessing Unusual Electronic Properties

INSTITUTION: Washington State University

PRINCIPAL INVESTIGATOR: G. A. Crosby

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ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

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A comprehensive program of synthesis, chemical characterization and optical investigation of complexes of  $(nd)^6$  configuration possessing charge-transfer (CT) excited states was carried out. Approximately sixty molecules of Ru(II) and Os(II) were examined, a dozen of Ir(III) and six of Pt(IV). Absorption spectra (300 and 77 K), luminescence spectra (77 - 1.5 K) and temperature dependent decay times, quantum yields and emission spectra were examined. Several systems were subjected to intense magnetic fields at low temperatures. Group theoretical models for the CT excited states of Ru(II) and Os(II) complexes were devised for systems of  $D_3$  and  $D_{2d}$  symmetry. A new criterion was found for classifying  $d\pi^*$  and  $\pi\pi^*$  states employing Ir(III) complexes and a configuration-interaction model for rationalizing  $d\pi^*-\pi\pi^*$  interactions in complexes was devised.

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Several new luminescent systems useful for photochemical energy donors were discovered. The project carried the laboratory significantly further toward its stated goal of defining the principles by which new substances with potential value as media for electrooptical devices can be designed and synthesized in the laboratory.

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### Summary of Effort

Characterization of CT Excited States of Ru(II) and Os(II) complexes.

Our work in this area was essentially completed. For the Ru(II) systems we completed the spectroscopic work on several series of mixed-ligand chelates and proposed a complete comprehensive group-theoretic and orbital promotional model for both  $D_3$  and  $D_{2d}$  symmetries (See publication list #'s 49, 52, 53, 54).

For Osmium(II) we completed both the synthetic and optical studies on complexes of  $D_3$  symmetry and the results are in publishable form (50,51). We established beyond reasonable doubt the prominent role played by spin-orbit coupling in controlling the optical behavior of these materials. Several new and potentially useful complexes were discovered.

### Magnetic Field Interactions

As originally proposed we subjected several types of complexes to intense magnetic fields in a search for field-dependent optical phenomena. For  $K_2Pt(CN)_6$  positive results were obtained (see Progress Report (PR) #2), but for the  $[Ru(II)(NH_3)_5L]^{+2}$  systems no H effect on photochemical processes was discovered [The preliminary result reported in PR#3 was in error]. These experiments were eventually abandoned.

A search for a magnetic effect on the optical properties of Ir(III) complexes was carried out. No significant effect was observed.

### Spectroscopic Studies of $d^{10}$ Complexes

A comprehensive program of synthesis, characterization, and optical investigation of  $d^{10}$  systems was completed. The studies were extremely fruitful and one manuscript is in preparation (57). The work on these systems is still preliminary, however, and has become the basis for several current investigations in the laboratory.

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### Characterization of Iridium(III) Excited States

Several new Ir(III) molecules were subjected to detailed optical investigations at low temperatures. An additional new criterion for classifying CT excited states was discovered, and a new prototype molecule for CT emission was proposed (55).

A series of solvent perturbation studies was carried out and a semiquantitative model for describing  $d\pi^*-\pi\pi^*$  interaction in complexes was developed (56).

### Rare Earth Chelates

Optical studies on rare earth chelates were made at 77°-4°K. The results showed a clean decoupling of a high energy excited state from the lowest singlet (triplet?) as revealed in the excitation spectra. These studies are not yet complete. The work accomplished is described in PR#4.

### Optical Manifestations of Solid State Interactions

Our search for substances exhibiting substantial solid state interactions as revealed by optical methods ranged from very promising  $[\text{phenH}]^+[\text{Ir(III)(phen)}_4]^-$  to negative results  $[\text{Zn(N-N)(S-S)}]$ . We have been led to investigate new types of materials, however, and such studies form a considerable part of a new proposal to AFOSR.

### Laboratory Improvements

During the tenure of the grant, giant strides were made in updating the laboratory. A new Data Acquisition System was designed, purchased, and put into operation. A Molectron  $\text{N}_2$  Pulsed Laser and associated Dye Laser were installed. A new Raman Laser system was acquired, and a new IR instrument was purchased (the latter has not yet been delivered). In addition, most of the instruments were interfaced to the PDP-11 and a Cromemco microprocessor was added to control the Raman (and IR) apparatus.

During the grant period the stated objectives of the entire research program did not change. The main intent was (and still is) to investigate new materials that were expected to display excited state properties of potential use in electrooptical devices. This objective was coupled to the parallel (and necessary) one of elucidating the fundamental properties of excited states such that criteria can be established to allow the design of technologically valuable materials at the molecular level. Considerable progress toward this objective was made (see publication list).

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## PUBLICATIONS

Cumulative List of AFOSR-supported Publications

- \* Reprints of article and DD 1473 sent to AFOSR.
- \* 1. G. A. Crosby, W. G. Perkins, and D. M. Klassen, "Luminescence From Transition-Metal Complexes: Tris(2,2'-bipyridine)- and Tris(1,10-phenanthroline)ruthenium(II)," Journal of Chemical Physics 43, 1498 (1965).
- \* 2. G. A. Crosby, "Luminescent Organic Complexes of the Rare Earths," a review, Molecular Crystals 1, 37 (1966).
- \* 3. G. A. Crosby, D. M. Klassen, and S. L. Sabath, "Intramolecular Energy Transfer in Osmium(II) Complexes," Molecular Crystals 1, 453 (1966).
- \* 4. G. A. Crosby, "Optical Excitation of Transition-Metal Ions Via Intramolecular Energy Transfer," Journal de Chimie Physique 64, 160 (1967).
- \* 5. D. M. Klassen and G. A. Crosby, "Reassignment of the Luminescence From Ruthenium(II) Complexes," Chemical Physics Letters 1, 127 (1967).
- \* 6. D. M. Klassen and G. A. Crosby, "Ligand-Field Transitions in Tertiary Phosphine and Arsine Complexes of Ruthenium(II) and Osmium(II)," Journal of Molecular Spectroscopy 25, 398 (1968).
- \* 7. D. M. Klassen and G. A. Crosby, "Spectroscopic Studies of Ruthenium(II) Complexes. Assignment of the Luminescence," Journal of Chemical Physics 48, 1853 (1968).
- 8. G. A. Crosby and R. D. Caton, "Review of Fluorescence and Phosphorescence Analysis: Principles and Applications edited by D. M. Hercules," Journal of the Franklin Institute 285, 93 (1968).
- \* 9. J. N. Demas and G. A. Crosby, "On the Multiplicity of the Emitting State of Ruthenium(II) Complexes," Journal of Molecular Spectroscopy 26, 72 (1968).
- \* 10. G. A. Crosby and D. H. W. Carstens, "Luminescence From Rhodium(III) and Iridium(III) Complexes," Molecular Luminescence, ed. E. C. Lim, W. A. Benjamin, 1969, p. 309.
- \* 11. J. N. Demas, T. F. Turner, and G. A. Crosby, "Preparation and Thin-Layer Chromatography of cis-Dicyanobis(2,2'-bipyridine)ruthenium(II)," Inorganic Chemistry 8, 674 (1969).
- \* 12. D. H. W. Carstens and G. A. Crosby, "Luminescence From Complexes of Rhodium(III)," Journal of Molecular Spectroscopy 34, 113 (1970).
- \* 13. R. W. Harrigan and G. A. Crosby, "Temperature Dependence of the Luminescence of  $Tb^{3+}$  Complexes," Journal of Chemical Physics 52, 4912 (1970).
- \* 14. G. A. Crosby and B. Pankuch, "Cryostat for Spectroscopic Measurements of Solutions and Rigid Glasses," Chemical Instrumentation 2, 329 (1970).



## PUBLICATIONS - continued

- \* 15. J. N. Demas and G. A. Crosby, "Photoluminescence Decay Curves: An Analysis of the Effects of Flash Duration and Linear Instrumental Distortions," Analytical Chemistry 42, 1010 (1970).
- \* 16. R. W. Harrigan and G. A. Crosby, "Variable Temperature Sample Mount for Luminescent Powders," Spectrochimica Acta 26A, 2225 (1970).
- \* 17. J. N. Demas and G. A. Crosby, "Quantum Efficiencies of Transition-Metal Complexes. I. d-d Luminescence," Journal of the American Chemical Society 92, 7262 (1970).
- \* 18. G. A. Crosby, R. J. Watts, and D. H. W. Carstens, "Inversion of Excited States of Transition-Metal Complexes," Science 170, 1195 (1970).
- \* 19. R. J. Watts, R. W. Harrigan, and G. A. Crosby, "Temperature and Magnetic Field Effects on the Luminescence Lifetimes of Complexes of Ruthenium(II) and Iridium(III)," Chemical Physics Letters 8, 49 (1971).
- \* 20. T. R. Thomas and G. A. Crosby, "Luminescence From Rhodium(III) Ammine Complexes," Journal of Molecular Spectroscopy 38, 118 (1971).
- \* 21. J. N. Demas and G. A. Crosby, "The Measurement of Photoluminescence Quantum Yields. A Review," Journal of Physical Chemistry 75, 991 (1971).
- \* 22. J. N. Demas and G. A. Crosby, "Quantum Efficiencies of Transition-Metal Complexes. II. Charge-Transfer Luminescence," Journal of the American Chemical Society 93, 2841 (1971).
- \* 23. R. J. Watts and G. A. Crosby, "Spectroscopic Characterization of Complexes of Ruthenium(II) and Iridium(III) with 4,4'-Diphenyl-2,2'-bipyridine and 4,7-Diphenyl-1,10-phenanthroline," Journal of the American Chemical Society 93, 3184 (1971).
- 24. G. A. Crosby, R. W. Harrigan, and R. J. Watts, "Optical Measurement of Temperature," Patent Applied For.
- \* 25. G. A. Crosby, R. J. Watts, and S. J. Westlake, "Phosphorescence of Acetylacetonates of Trivalent Metals," Journal of Chemical Physics 55, 4663 (1971).
- \* 26. R. J. Watts and G. A. Crosby, "Quantum Efficiencies of Transition-Metal Complexes. III. The Effect of Ligand Substituents on Radiative and Radiationless Processes," Journal of the American Chemical Society 94, 2606 (1972).
- \* 27. R. J. Watts and G. A. Crosby, "A Comparison of  $n\pi^*$ - $\pi\pi^*$  Interactions in Aromatics with  $d\pi^*$ - $\pi\pi^*$  Interactions in Iridium(III) Complexes," Chemical Physics Letters 13, 619 (1972).



## PUBLICATIONS - continued

- \* 28. R. J. Watts, G. A. Crosby, and J. L. Sansregret, "Excited States of Transition-Metal Complexes. A Spectroscopic Measurement of  $d\pi^*-\pi\pi^*$  Interactions in Iridium(III) Complexes," Inorganic Chemistry 11, 1474 (1972).
- 29. G. A. Crosby, J. N. Demas, and J. B. Callis, "Absolute Quantum Efficiencies," a review
- \* Journal of Research, National Bureau of Standards, 76A, 561 (1972) and in the Proceedings of the Conference on Accuracy in Spectrophotometry and Luminescence Measurements, NBS, Gaithersburg, Maryland, March 22-24, 1972. (NBS Special Publication 378, May 1973, p. 151).
- \* 30. T. R. Thomas, R. J. Watts, and G. A. Crosby, "Radiative and Radiationless Decay Processes in Rhodium(III) Ammine Complexes," Journal of Chemical Physics, 59, 2123 (1973).
- \* 31. R. W. Harrigan, G. D. Hager, and G. A. Crosby, "Evidence for Multiple-State Emission from Ruthenium(II) Complexes," Chemical Physics Letters, 21, 487 (1973).
- \* 32. R. W. Harrigan and G. A. Crosby, "Symmetry Assignments of the Lowest CT Excited States of Ruthenium(II) Complexes via a Proposed Electronic Coupling Model," Journal of Chemical Physics, 59, 3468 (1973).
- \* 33. G. A. Crosby, K. W. Hipps, and W. H. Elfring, Jr., "On the Appropriateness of Assigning Spin Labels to Excited States of Inorganic Complexes," Journal of the American Chemical Society, 96, 629 (1974).
- \* 34. J. L. Sansregret and G. A. Crosby, "Molecular Sieves as Media for Growing Crystals," Journal of Crystal Growth, 21, 313 (1974).
- \* 35. K. W. Hipps and G. A. Crosby, "Geometrical Distortion and Spin-Orbit Splitting in Excited Transition-Metal Complexes," Inorganic Chemistry, 13, 1543 (1974).
- \* 36. D. C. Baker and G. A. Crosby, "Spectroscopic and Magnetic Evidence for Multiple-State Emission from Tris(2,2'-bipyridine)ruthenium(II) Sulfate," Chemical Physics, 4, 428 (1974).
- \* 37. G. A. Crosby, G. D. Hager, K. W. Hipps, and M. L. Stone, "Investigation of the Temperature Dependence of Ruthenocene Photoluminescence," Chemical Physics Letters, 28, 497 (1974).
- \* 38. G. D. Hager and G. A. Crosby, "Charge-Transfer Excited States of Ruthenium(II) Complexes. I. Quantum Yield and Decay Measurements," Journal of the American Chemical Society, 97, 7031 (1975).
- \* 39. G. D. Hager, R. J. Watts, G. A. Crosby, "Charge-Transfer Excited States of Ruthenium(II) Complexes. II. Relationship of Level Parameters to Molecular Structure," Journal of the American Chemical Society, 97, 7037 (1975).

## PUBLICATIONS - continued

- \* 40. K. W. Hipps and G. A. Crosby, "Charge-Transfer Excited States of Ruthenium(II) Complexes. III. An Electron-Ion Coupling Model for  $d\pi^*$  Configurations", Journal of the American Chemical Society, 97, 7042 (1975).
- \* 41. G. A. Crosby, "Spectroscopic Investigations of Excited States of Transition-Metal Complexes", Accounts of Chemical Research, 8, 231 (1975).
- \* 42. G. A. Crosby, "Luminescence as a Probe of Excited State Properties", Advances in Chemistry (Proceedings of the Symposium on Inorganic Compounds with Unusual Properties, University of Georgia, Jan. 1975, Ed., R. B. King) No. 150, American Chemical Society, 1976, Chapter 13.
- \* 43. G. A. Crosby and W. H. Elfring, Jr., "Excited States of Mixed Ligand Chelates of Ruthenium(II) and Rhodium(III)", Journal of Physical Chemistry (Proceedings of the Michael Kasha Symposium on Energy Transfer in Organic, Inorganic, and Biological Systems, Florida State University, Jan. 1976), 80, 2206 (1976).
- \* 44. K. W. Hipps, G. A. Merrell, G. A. Crosby, "Geometrical Distortion of the Excited States of  $d^6$  Transition Metal Complexes: Systems of  $O$  and  $D_4$  Symmetry", Journal of Physical Chemistry (Proceedings of the M. Kasha Symposium), 80, 2232 (1976).
- \* 45. K. W. Hipps, "The Molecular Theory of Polarized Emission: Linear, Circular, and Magnetically Induced Circular Polarization of Emission", Chemical Physics, 23, 451 (1977).
- \* 46. K. W. Hipps and G. A. Crosby, "Magnetically Induced Circular Polarization of Emission: Application to Inorganic Complexes", Optical Engineering, 17, 176 (1978); also published in the Proceedings of the 21st Annual Symposium of the Society of Photo-optical and Instrumentation Engineers, San Diego, August 22-27, 1977 [SPIE, 112, 132 (1977)].
- \* 47. D. C. Baker, K. W. Hipps, G. A. Crosby, "Infrared-Optical Double Resonance and Thermal Modulation Spectroscopy of the Tris(2,2'-Bipyridine)ruthenium(II) Cation", Chemical Physics Letters, 53, 333 (1978).
- \* 48. K. W. Hipps and G. A. Crosby, "Applications of the Photoelastic Modulator to Polarization Spectroscopy", Journal of Physical Chemistry, 83, 555 (1979).

49. W. H. Elfring, Jr. and G. A. Crosby, "Excited States of Mixed-Ligand Chelates of Ruthenium(II): Quantum Yield and Decay Time Measurements", Journal of Physical Chemistry, submitted.

The photoluminescence of a series of  $[\text{Ru(II)(bpy)}_m(\text{N-N})_n]^{2+}$  cations [ $m = 3 - n$ ;  $n = 0, 1, 2, 3$ ;  $\text{bpy} = 2,2'$ -bipyridine;  $\text{N-N} = 1,10$ -phenanthroline (phen) or substituted-phen or substituted-bpy] was investigated. All compounds displayed a prominent visible luminescence, a single  $\sim 1.3$  kK vibrational progression, and an  $\sim 5$   $\mu\text{sec}$  decay time at 77 K that increased monotonically as the temperature was lowered. Quantum yields at 77 K ranged between 0.35 - 0.58. The data were analyzed in terms of a charge-transfer-to-ligand excited manifold of three levels. No conclusive evidence for an electronic symmetry lower than  $D_3$  was found.

50. B. J. Pankuch, D. E. Lacky, G. A. Crosby, "Charge-Transfer Excited States of Osmium(II) Complexes: I. Assignment of the Visible Absorption Bands", Journal of Physical Chemistry, submitted.

The visible and near-uv absorption and photoluminescence spectra of five tris and five bis complexes of osmium(II) containing  $\pi$ -conjugated ligands have been assigned to charge-transfer-to-ligand excited configurations. For the trigonal molecules both the emission bands and the weak absorption bands lying contiguous to them have been assigned symmetry labels based on an ion-parent coupling model previously developed for the analogous states of ruthenium(II) complexes. Substantial d-orbital penetration from osmium(II) onto the ligand  $\pi$ -system is deduced from the optical measurements. Similarities and differences between analogous sets of osmium(II) and ruthenium(II) species are discussed.

51. D. E. Lacky, B. J. Pankuch, G. A. Crosby, "Charge-Transfer Excited States of Osmium(II) Complexes: II. Quantum Yield and Decay Time Measurements", Journal of Physical Chemistry, submitted.

Computer analysis of the temperature dependence ( $\sim 4$ -77 K) of the intensity and decay time of the photoluminescence observed from five tris osmium(II) complexes containing  $\pi$ -conjugated ligands has yielded energy level gaps and both radiative and radiationless decay constants for the lowest emitting levels. The derived empirical parameters have been rationalized on the basis of an ion-parent coupling model previously invoked to describe the optical behavior of the analogous ruthenium(II) complexes. The three emitting levels have been assigned to a  $d\pi^*(a_2)$  charge-transfer configuration with  $A_1$ , E, and  $A_2$  symmetries in the group  $D_3$ .



52. M. L. Stone and G. A. Crosby, "Assignment of the Visible Charge-Transfer Bands of  $D_{2d}$  Bis Complexes of Ruthenium(II)," tentative.

A systematic spectroscopic study of complexes of Ru(II) with 2,2',2''-terpyridine, 4'-phenyl-2,2',2''-terpyridine (tro), and 4,4',4''-triphenyl-2,2',2''-terpyridine (tsite) by absorption and emission methods was carried out. The measurements included variable low temperature luminescence and decay time measurements (77-4°K) and photoselection experiments. Aided by comparison spectra from analogous Fe(II) and Os(II) complexes we were able to account for all the major visible absorption bands, the unique temperature dependences of the emission spectra and the polarization data. The analysis is based on  $D_{2d}$  symmetry and spin-orbit coupling of the lowest level was invoked to rationalize the temperature dependence of the observed emission intensities and decay times.

53. M. L. Stone and G. A. Crosby, "Quantum Yields and Decay Times of  $D_{2d}$  Bis Ruthenium(II) Complexes Containing N-Heterocyclic Ligands," tentative.

The thermal dependences of the optical quantum yields and decay times of three complexes with  $D_{2d}$  symmetry were investigated in the range of (77-4K). Analysis by computer revealed multiple luminescing states that point to substantial spin-orbit coupling in the lowest (emitting) term. The origin of the luminescence was assigned to the split components of the (CTTL)  $^3E$  term.

54. M. L. Stone and G. A. Crosby, "Spectroscopic Properties of Mixed-Ligand Chelates of Ruthenium(II) Containing N-Heterocyclic Ligands: Evidence for Ring-Localized Charge Transfer Excited States," tentative.

Fourteen tris ruthenium(II) complexes containing bidentate nitrogen heterocyclic ligands were synthesized, purified, and studied spectroscopically. The complexes comprised two series, namely  $[Ru(L1)_m(L2)_n]^{2+}$  [ $L1 = 2,2'$ -biquinoline or 2-(2'-pyridyl)quinoline;  $L2 = 2,2'$ -bipyridine, 1,10-phenanthroline, 2-(2'-pyridyl)quinoline, or 4,4'-dimethyl-2,2'-bipyridine;  $m = 3, 2, 1$  and  $n = 3 - m$ ]. Room temperature absorption spectra in methanol of the ligands and complexes were recorded, and the peak frequencies and intensities tabulated. All of the complexes were highly colored solids and exhibited strong charge transfer (CT) absorption bands in the visible region. The emission spectra of the bidentate ligands in ethanol-methanol (4:1, v/v) at 77 K showed mainly  $\pi-\pi^*$  phosphorescence.

Temperature dependences of the emission spectra (2 - 77 K) and decay times were recorded. All the measured decay times were exponential in the temperature range 2 to 77 K. They all increased from their 2-10  $\mu\text{sec}$  values at 77 K to 50-350  $\mu\text{sec}$  at 2 K, implying emission from a manifold of thermally equilibrated levels.

Absolute quantum yields at 77 K in ethanol-methanol (4:1, v/v) relative to fluorescein were measured. The values ranged from 48% for  $[Ru(2,2',2''\text{-terpyridine})_2]^{2+}$  to 2% for  $[Ru(2,2'\text{-biquinoline})_2(4,4'\text{-dimethyl-2,2'-bipyridine})]^{2+}$ .



The luminescing states of the Ru(II) compounds were characterized as charge transfer. However, within either of the two tris chelate series investigated, the observed properties of a mixed-ligand complex could not be rationalized on the basis of a simple weighted average of the observed optical properties of the tris parent species. The possible roles of orbital splittings and steric hindrance in dictating the optical properties were discussed.

55. T. L. Cremers and G. A. Crosby, "Cis-Dichloro-Bis-bipyridine Iridium(III): A Model Charge Transfer Emitter," tentative.

The chelate cis-dichloro-bis-bipyridine Iridium(III) is proposed as a new prototype system displaying charge-transfer luminescence. At 77°K the effect of solvent perturbations on the observed luminescence parallels that of the previously proposed standard CT emitter cis-dichloro-bis 1,10 phenanthroline Iridium(III), but, as the temperature is lowered to 4°K, disparate behavior is evident. The latter molecule clearly displays a solvent dependence of the lifetime vs. temperature curves that signals strong  $d\pi^*-\pi\pi^*$  interaction, whereas the newly proposed standard CT emitter displays  $\tau$  vs. T curves that are virtually solvent independent and characteristic of emission from a manifold of genuine CT excited states.

56. T. L. Cremers and G. A. Crosby, "Reordering of the Lowest Excited States of some Bis-Chelated Iridium(III) Complexes by Ligand Modifications and Solvent Perturbations," tentative.

The character of the emitting state of some iridium(III) 1,10-phenanthroline and 2,2'-bipyridine complexes can be altered by proper choice of ligands. The emission from  $[\text{IrCl}_2(4,4'\text{-dimethyl-2,2'-bipyridine})_2]\text{Cl}$  is believed to arise from a state almost purely metal-to-ligand charge transfer in character. In contrast, a ligand localized state is proposed as the emitting state for  $[\text{IrCl}_2(5,6\text{-dimethyl-1,10-phenanthroline})_2]\text{Cl}$  and a state with mixed charge transfer and ligand character is believed to be responsible for the emissions from  $[\text{IrCl}_2(1,10\text{-phenanthroline})_2]\text{Cl}$ . The effects of solvent medium and temperature (2-77 K) on the emission characteristics of these complexes were examined and were used as probes for assigning the nature of the lowest excited states. The data are interpreted in terms of a configuration interaction model.

57. K. A. Truesdell and G. A. Crosby, "Spin-Orbit Coupling in Zn(II) and Cd(II) Complexes," tentative.

Studies of relative phosphorescence to fluorescence yields ( $\phi_p/\phi_f$ ) of a series of complexes of the formula  $\text{M}(\text{N-N})\text{X}_2$  have been carried out at 77 K. The results show a clear dependence of  $\phi_p/\phi_f$  on the spin-orbit coupling parameters of both the metal ions and the coordinated halides. The relevance of this information to radiationless transition probabilities in non-halogen containing complexes exhibiting interligand transmetallic charge transfer excited states is discussed.

Dissertations Completed During Grant Tenure

M. S. Pearce, "A Study of the Optical Properties of Group VIB Carbonyl Complexes" (1977).

K. A. Truesdell, "Spectroscopic Investigations of the Excited States of Zinc(II) Complexes" (1978).

T. L. Cremers, "Photophysical Studies of Ruthenium(II) and Iridium(III) Complexes Displaying Charge Transfer Excited States" (Completed 8/79; degree to be awarded officially June 1980).

M. L. Stone, "Excited States of Ruthenium(II) Bis and Tris Complexes Containing N-Heterocyclic Ligands" (Completed 9/79; degree to be awarded officially June 1980).

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A comprehensive program of synthesis, chemical characterization and optical investigation of complexes of (nd) <sup>6</sup> configuration possessing charge-transfer (CT) excited states was carried out. Approximately sixty molecules of Ru(II) and Os(II) were examined, a dozen of Ir(III) and six of Pt(IV). Absorption spectra (300 and 77 K), luminescence spectra (77 - 1.5 K) and temperature dependent decay times, quantum yields and emission spectra were examined.		



## 20. Abstract (continued)

Several systems were subjected to intense magnetic fields at low temperatures. Group theoretical models for the CT excited states of Ru(II) and Os(II) complexes were devised for systems of  $D_3$  and  $D_{2d}$  symmetry. A new criterion was found for classifying  $d\pi^*$  and  $\pi\pi^*$  states employing Ir(III) complexes and a configuration-interaction model for rationalizing  $d\pi^*-\pi\pi^*$  interactions in complexes was devised.

Several new luminescent systems useful for photochemical energy donors were discovered. The project carried the laboratory significantly further toward its stated goal of defining the principles by which new substances with potential value as media for electrooptical devices can be designed and synthesized in the laboratory.